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Preliminary Communication

Chelating diphos ligands with inorganic backbones. Crystal structure of $[PtCl_2\{(PPh_2O)_2SiPh_2\}]$

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Abstract

The reaction between $[PtCl_2(PPh_2OH)_2]$ (**1**) and $SiCl_2Ph_2$ gives the platinum silyldiphosphinite complex $[PtCl_2\{(PPh_2O)_2SiPh_2\}]$ (**2**), the X-ray crystal structure of which has been determined. Treatment of **1** with $SnCl_2Ph_2$ gives the complex $[NHEt_3][PtCl_2\{(PPh_2O)_2SnClPh_2\}]$ (**3**).

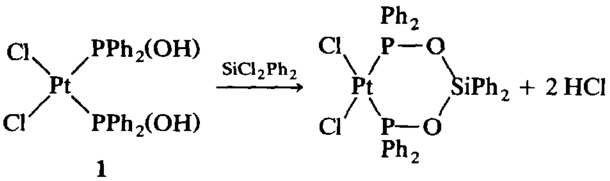
Key words: Platinum; Silicon; Chelate; Phosphinite; Crystal structure

1. Introduction

Though diphosphines have been important ligands for synthesis and homogeneous catalysis for at least 30 years [1], it is only comparatively recently that other chelating phosphorus ligands containing phosphite [2] and phosphinite [3] donors have attracted attention as ligands. We were interested in the possibility of obtaining complexes containing two phosphinite ligands capable of forming six-membered chelates because analogous diphosphine chelates of palladium(II) are excellent catalysts for polyketone synthesis by CO/C_2H_4 copolymerization [4]. We report here diphosphinite chelates featuring entirely inorganic backbones synthesized using a platinum(II) template; previously other workers have shown [5] that diphosphinites can be synthesized using a molybdenum(0) template.

2. Results and Discussion

The complex *cis*-$[PtCl_2(PPh_2OH)_2]$ (**1**) [6] reacts with one equivalent of $SiCl_2Ph_2$ in CH_2Cl_2 over 0.5 h to give the new silyldiphosphinite complex $[PtCl_2\{(PPh_2O)_2SiPh_2\}]$ (**2**) quantitatively (eqn. 1), as shown



1 **2**

(1)

by ^{31}P, ^1H and ^{13}C NMR NMR spectroscopy [7*]. Crystals of **2** were grown from CH_2Cl_2/Et_2O and X-ray crystallography [8*] revealed the molecular structure shown in Fig. 1. The platinum has a square planar environment (mean deviation from the $PtCl_2P_2$ mean plane = 0.0755 Å) and the silyldiphosphinite ligand chelates the metal with the expected *cis* geometry, leading to approximate molecular mirror symmetry. The bite angle in **2** (P(2)–Pt(1)–P(1) 96.7(1)°) is large when compared to that for $[PdCl_2(PPh_2(CH_2)_3PPh_2)]$ (90.58(5)°) [9], which has an alkyl backbone. The bite angle of diphosphine ligands has been identified as important in controlling catalytic reactions [10]. The flexibility about the backbone oxygen atoms is reflected in the large deviations from tetrahedral geometry in the internal bond angles of the chelate ring (P(2)–O(1)–Si = 130.4(2)°, O(1)–Si–O(2) = 103.4(2)°, P(1)–O(2)–Si = 133.2(2)°). The 6-membered ring conformation in **2** can be described as a boat flattened at Pt(1) (see Fig. 1). The angles between the P(1)–P(2)–O(1)–O(2) mean plane and the $PtCl_2P_2$ and O(1)–Si(1)–O(2) mean planes are 15.5° and 35.8° respectively.

The formation of silyldiphosphinite complexes in this manner is sensitive to the nature of the substituents on silicon. It was shown by ^{31}P NMR spectroscopy that $SiCl_2{}^tBu_2$ does not react with **1** over 1 h even in the presence of a five-fold excess of triethylamine. In contrast, $SiCl_2Me_2$ reacted readily with **1** in the absence of triethylamine with evolution of HCl to give a white precipitate that was too insoluble for further characterization. It is possible that this product is the polymeric species $[PtCl_2\{(PPh_2O)_2SiMe_2\}]_n$, though elemental analysis showed it to be of variable

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* Reference number with an asterisk indicates a note in the list of references.

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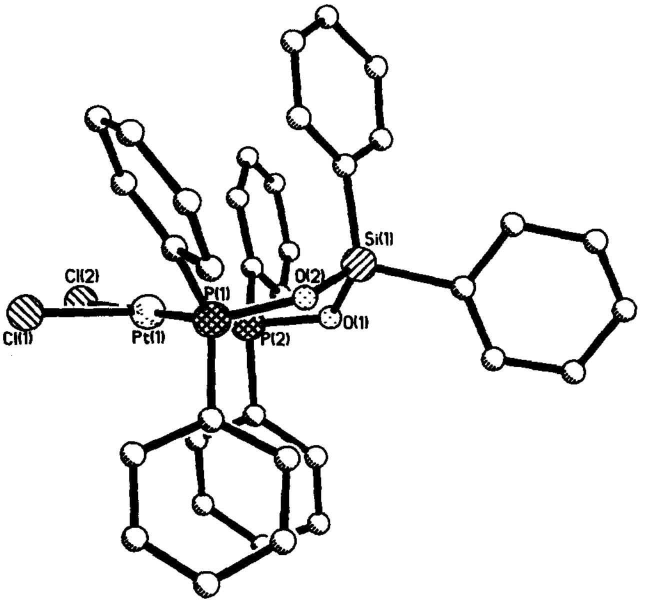

Fig. 1. Molecular structure of 2 showing atom labelling. Important molecular dimensions include: bond lengths (Å) Pt-P(1) 2.232(1), Pt-P(2) 2.228(1), Pt-Cl(1) 2.370(1), Pt-Cl(2) 2.360(1); torsion angles (°) P(2)-Pt(1)-P(1)-O(2) 23.5, P(1)-Pt(1)-P(2)-O(1) −14.4, Pt(1)-P(2)-O(1)-Si(1) −27.1, O(2)-Si(1)-O(1)-P(2) 55.7, Pt(1)-P(1)-O(2)-Si(1) 4.5, O(1)-Si(1)-O(2)-P(1) −42.3.

composition. Kee *et al.* [10] have recently isolated the related free ligand $\{(4\text{-}CH_3C_6H_4)_2PO\}_2SiMe_2$.

$SnCl_2Ph_2$ reacts smoothly with complex **1** in CH_2Cl_2 in the presence of triethylamine to give a new species **3** (eqn. 2) as the only phosphorus-containing product

$$[PtCl_2(PPh_2OH)_2] + 2\,NEt_3 + SnCl_2Ph_2 \longrightarrow \underset{\mathbf{3}}{[PtCl_2\{(PPh_2O)_2SnClPh_2\}]^-} + NEt_3H^+ + NEt_3HCl \qquad (2)$$

[12*]. The structure of **3** was assigned on the basis of (i) satisfactory elemental analysis; (ii) the presence of ^{119}Sn satellites in the ^{31}P NMR spectrum; (iii) the ^1H NMR spectrum, which showed the presence of one $HNEt_3^+$ per six phenyl groups, suggesting that the complex was a monoanion; (iv) the ^{119}Sn NMR spectrum which in CD_2Cl_2 was a triplet at $\delta(Sn) = 86.2$ ppm, consistent with the presence of five coordinate tin(IV) [13]. The Lewis acidity of the central Sn in the backbone is an interesting feature of the ligand: in neat C_5D_5N the ^{119}Sn resonance is broadened ($w_{1/2} = 600$ Hz) and moves to 21 ppm, suggesting that the Cl on the Sn can be displaced by pyridine.

It has been shown that silyldiphosphinites or stannyldiphosphinites can be readily synthesised within the coordination sphere of platinum. The possibility is under investigation of extending this reaction to the synthesis of chelates with other metals (*e.g.* Pd) to obtain novel inorganic heterocycles containing other Lewis acid sites in the backbone (*e.g.* Ti).

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7 Characterization of 2: ^{31}P NMR (162 MHz), $\delta(P)$ 73.9, $^1J(PtP)$ 4053 Hz; ^1H NMR (270 MHz) δ 7.21–7.29 (m), 7.32–7.40 (m), 7.44–7.52 (m), 7.78–7.86 (m); $^{13}C\text{-}\{^1H\}$ (67.5 MHz) δ 134.2 (s), 133.0 (m), 132.0 (s), 131.9 (s), 128.8 (s), 128.2 (s), 128.1 (t, 6.1 Hz) 127.9 (s).

8 Crystal Data for 2: $C_{26}H_{30}Cl_2O_2P_2PtSi$, M = 850.6, monoclinic, space group $P2_1/n$ (non-standard No. 14), $a = 10.38(3)$ $b = 16.528(4)$, $c = 17.649(4)$ Å, $\beta = 95.24(2)°$, $V = 3395(2)$ Å^3, $Z = 4$, $D_x = 1.664$ gcm^{-3}, $\bar{\lambda} = 0.71073$ Å, $\mu = 44.5$ cm^{-1}, $F(000) = 1672$, T = 295 K. Data were collected on a Siemens R3m diffractometer for a unique portion of reciprocal space for $4 < 2\theta < 50°$. The

structure was solved by heavy atom methods and refined by least-squares against F data to $R = 0.026$ and $wR = 0.036$, $S = 0.99$ for 6283 unique, absorption corrected, observed ($I > 2\sigma(I)$) intensity data. Atomic coordinates, bond lengths, bond angles and displacement parameters for **2** have been deposited with the Cambridge Crystallographic Data Centre.

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12 Characterization of **3**: Elemental analysis (calc.) C, 46.8 (46.8), H, 4.6 (4.2), N, 1.3 (1.3); ^{31}P-{^{1}H} NMR (36.2 MHz) $\delta(P) = 56.3$ ppm, $^1J(PtP) = 4163$ Hz, $^2J(SnP) = 95$ Hz; ^{1}H NMR (270 MHz) δ 1.10 (t, 7.5 Hz, 9H), 2.87 (q, 7.5 Hz, 6H), {7.01–7.38 (m), 7.68–7.92 (m)} (30H), 8.90 (s, 1H).

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